Indian J. Phys. **54B**, 106–111 (1980)

A semi-classical treatment of Laser-induced multiphoton excitation of polyatomic molecules

Manju Prakash

Multidisciplinary Research Section, Bhabha Atomic Research Centre, Trombay, Bombay-400085.

Abstract. A semi-classical theory of the multiphoton excitation of polyatomic molecules under infrared laser radiation is presented. By assuming the molecule to be a truncated anharmonic oscillator with N discrete levels, we solve the time-dependent Schrodinger equation. The laser field which couples the states of the molecule is represented by a time-dependent driving field $E_0 \cos \omega t$. Rotating wave approximation is used and general expressions are derived for the occupational probabilities for various levels and the average energy absorbed by the molecule over the duration of a laser pulse.

By taking SF_6 as a representative molecule with the parameters corresponding to its ν_3 mode and a CO_2 laser, we have obtained the absorption curve for various laser powers.

1. Introduction

Much interest in the process of collisionless multiphoton dissociation of the polyatomic molecules by CO_2 laser radiation has been aroused by the demonstration of the isotopic selectivity of the process (Ambartzumian *et al* 1974, Lyman *et al* 1974). The exact mechanism whereby, upwards of thirty photons energetically needed for dissociation can be absorbed by a single molecule in a short time, is of fundamental interest. Therefore, it is this physical aspect of the phenomenon that we emphasize in this paper.

Bloembergen (1975) forwarded a model of polyatomic molecule in which the low lying vibration-rotation levels of the molecule are regarded at discrete. However, above some excitation, the molecular levels are assumed to form suddenly a quasi-continuum, where the density of vibrational states is very high. Though this model satisfactorily explains the absorption of a large number of photons in the quasi continuum, where octahedral splittings, rotational energy changes of coriolis coupling tend to compensate the anharmonicity, the discrete states at low excitation represent a possible bottleneck (Cantrell 1975, Latokhov 1976, Bloembergen 1976). In this paper we have computed the absorption curve of the ν_3 mode of the SF_6 molecule interacting with CO_2 laser. Our results yield some insight into the absorption mechanism in the discrete states. Though, similar studies have already been made by (Larsen 1976, Jortner 1976), our approach is much more amenable to computations than the previous attempts.

2. Theoretical framework of the absorption curve calculation

The time dependent molecular wave functions satisfy the equation

$$\frac{i\hbar\partial\psi(\boldsymbol{r}, t)}{\partial t} = H\psi(\boldsymbol{r}, t), \tag{1}$$

where, H denotes the perturbed Hamiltonian of the molecular system (SF_6) interacting with the electromagnetic field of the incident CO_2 laser. H can be split into H_o, the molecular Hamiltonian and the dipole interaction term $\overline{\mu}\,\overline{E}\cos\omega t$.

Here, ω is the frequency of the incident laser field.

We expand the perturbed time dependent wave function in terms of the eigenfunctions of the molecular Hamiltonian H_o.

$$\psi(\boldsymbol{r}, t) = \sum_n a_n(t)\phi_n(\boldsymbol{r})e^{-iE_nt/\hbar}. \tag{2}$$

With,

$$H_o\phi_n(\boldsymbol{r}) = E_n\phi_n(\boldsymbol{r}) \tag{3}$$

and $|a_n(t)|^2$, the probability of occupation of the nth vibrational state with energy E_n.

Substitution equation (2) in equation (1) and using the relation (3) we obtain,

$$a_n(t) = \frac{i}{\hbar}\sum_k (< n|\boldsymbol{\mu}.\boldsymbol{E}|k > \cos\omega t e^{i(E_n-E_k)t/\hbar})a_k(t). \tag{4}$$

In order to solve equation (4) we make the following assumptions :

(1) The discrete vibrational levels of the molecular Hamiltonian H_o constitute a set of N truncated, unevenly spaced energy levels, characterised by the energy spectrum given by

$$E_n = (n-1)\hbar\Omega+(n-1)(n-2)X_{33}\hbar\Omega$$
$$n = 1, 2 \ldots N \tag{5}$$

where, X_{33} is a measure of the vibrational anharmonicity of the molecule and Ω is the gound state absorption frequency (Larsen 1976).

(2) The dipole matrix element satisfies $< n|\boldsymbol{\mu}.\boldsymbol{E}|k > = 0$ unless $k = n\pm1$.

Using above, equation (4) reduces to,

$$a_n(t) = \frac{i}{\hbar}[\beta_{n-1}a_{n-1}(t)e^{i(\omega_{n-1}-\omega)t} + \beta_{n-1}a_{n-1}(t)e^{i(\omega_{n-1}+\omega)t} +$$
$$\beta_n a_{n+1}(t)e^{-i(\omega_n-\omega)t} + \beta_n a_{n+1}(t)e^{-i(\omega_n+\omega)t}]. \tag{6}$$

Here, $\beta_n = < n | \boldsymbol{\mu}.\boldsymbol{E} | n+1 >$ is the transition matrix element connecting the vibrational state n and $n+1$ and ω_n the corresponding frequency.

Since we are obviously interested in resonant phenomenon, it is further possible to simplify equation (6) by invoking rotating wave approximation. We then obtain

$$a_n(t) = \frac{i}{\hbar} [\beta_{n-1} a_{n-1}(t) e^{i(\omega_n - \omega)t} + \beta_n a_{n+1}(t) e^{-i(\omega_n - \omega)t}]. \tag{7}$$

The equation (7) can be solved by assuming a solution of the form

$$a_n(t) = \sum_{i=1}^{N} A_i f_n(\lambda_i) e^{i(\alpha_n + \lambda_i)t}$$

$$n = 1, 2 \ldots N \tag{8}$$

where, A_i, f_n and λ_i are to be determined and α_n is the overall anharmonicity of the n-th vibrational level, given by

$$\alpha_n = \left(\sum_{J=1}^{n-1} \omega_J - (n-1)\omega \right) \hbar. \tag{9}$$

Using equations (7) and (8), we obtain the recurrence relations determining $f_n(\lambda_i)$

$$2(\alpha_n + \lambda_i) f_n(\lambda_i) = \beta_{n-1} f_{n-1}(\lambda_i) + \beta_{n+1} f_{n+1}(\lambda_i)$$

$$n = 2, 3 \ldots N.$$

with

$$f_1(\lambda_i) = 1. \tag{10}$$

Since there is no $(N+1)$th level by our assumption $a_{N+1} = 0$ and hence

$$f_{N+1}(\lambda_i) = 0. \tag{11}$$

This is a polynomial equation determining N values of λ.

If at $t = 0$, we assume that all the molecules are in the ground state $n = 1$, then

$$a_n(0) = \sum_{i=1}^{N} A_i f_n(\lambda_i) = \delta_{n1}. \tag{12}$$

Relations (10) and (11) determine the solution (8) completely. The net energy absorbed by the molecule during the duration τ of the laser pulse is given by

$$E = \sum_{n=1}^{N} E_n P_n \tag{13}$$

where,

$$P_n = \frac{1}{\tau} \int_0^{\tau} |a_n(t)|^2 dt$$

is the average probability of occupation of the n-th vibrational state with energy E_n.

Using (10) P_n simplifies to—

$$P_n = \sum_{i=1}^{\infty} A_i^2 f_n^2(\lambda_i).$$

Here, the rapidly varying time dependent terms in equation (8) average out to zero on integration over the duration of the laser pulse.

We have developed a numerical algorithm to solve the equations (11) and (12) numerically. These solutions are then used to compute the average energy E absorbed by the molecule during its excitation by the laser pulse.

3. Results

We have obtained the absorption curves for the ν_3 vibrational mode of $^{32}SF_6$ molecule by calculating the average energy E absorbed by the mode for a wide range of the incident laser frequency. The vibrational energy spectrum of the ν_3 mode is assumed to be a truncated anharmonic oscillator with four discrete levels and obeying the relation (5) with $\hbar\Omega = 948.2$ cm^{-1} and $X_{33}\hbar\Omega = -1{\cdot}44$ cm^{-1}. For an allowed transition the matrix elements are assumed to be of simple harmonic oscillator type; i.e., $\beta_n = \sqrt{n}\beta_1$. Here $\beta_1 = \mu E = \hbar\omega_R$, is the ground state Rabi energy with ω_R the corresponding frequency. For a laser intensity of 4 MW/cm^2, $\omega_R = 0{\cdot}08$ cm^{-1}.

At $\omega_R = 0{\cdot}08$ cm^{-1}, we found that one photon transitions are more probable than the higher order ones. In fact the energy absorbed by the mode at the ground state resonant frequency is thousand times higher than that corresponding to the three photon transition frequency. At higher laser fields, $\hbar\omega_R = 0{\cdot}6$ cm^{-1}, higher order coherent transitions play a dominant role (Figure 1c). The different peaks in the absorption curve correspond to different orders of coherent excitation at a frequency ω determined by

$$n(\hbar\omega) = n\hbar\Omega + n(n-1)X_{33}\hbar\Omega$$
$$n = 1, 2, 3 \ldots \qquad (14)$$

X_{33} being negative in the equation (14) ω is less than Ω, and this explains qualitatively the red shift observed experimentally (Ambartzumian 1976).

As we increase the laser field further so that, $\hbar\omega_R \simeq X_{33}\hbar\Omega$ the power broadening effects (Ambartzumian 1976) overtake and the absorption peaks are broadened (Figures 1a and 1b). At still higher powers, $\hbar\omega_R \gg (\hbar\Omega)X_{33}$, the absorption characteristics are smeared out due to the dominant power broadening. At this power level the absorption phenomena can be well understood in terms of the classical mode (Bloembergen 1975).

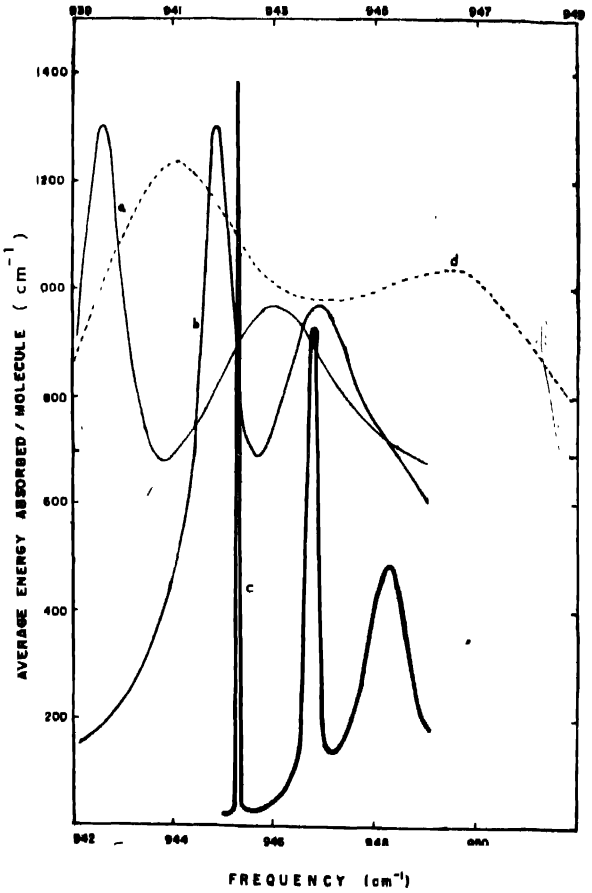

Figure 1. Frequency dependence of the average energy absorbed by the polyatomic molecule with $N = 4$, for various values of Rabi frequency ω_R and anharmonicity parameter $X_{33}\hbar\Omega$

a) $\hbar\omega_R = 1{\cdot}44\ \text{cm}^{-1} = -X_{33}\hbar\Omega$

b) $\hbar\omega_R = 2{\cdot}88\ \text{cm}^{-1} = -X_{33}\hbar\Omega$ (Upper abcissa)

c) $\hbar\omega_R = 0{\cdot}6\ \text{cm}^{-1}$, $X_{33}\hbar\Omega = -1{\cdot}44\ \text{cm}^{-1}$

d) $\hbar\omega_R = 10\ \text{cm}^{-1}$, $X_{33}\hbar\Omega = -2{\cdot}88\ \text{cm}^{-1}$ (Upper abcissa).

The widths of the resonances are broadened w.r.t. (b) due to power broadening effect.

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